

Second Semi-Annual Report

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Submitted by

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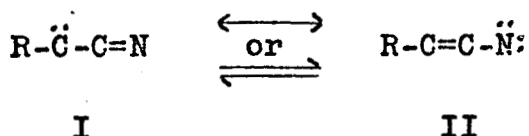
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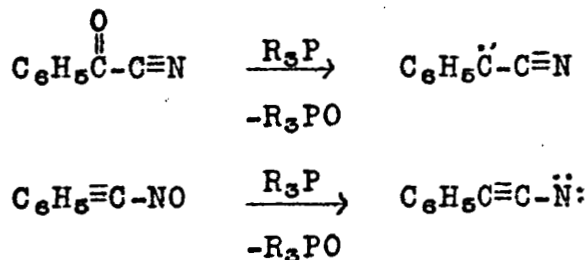
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Second Semi-Annual Report

Recognition (C. Ponnampuruma, 'Abiological Synthesis of Some Nucleic Acid Constituents', in The Origins of Prebiological Systems and of Their Molecular Matrices, Academic Press Inc., New York, 1965, p. 228) of cyanocarbenes as possible intermediates in the formation of proteins, purines and other compounds of biological significance (R. M. Kliss and C. N. Matthews, Proc. Nat'l. Acad. Sci. U. S. 48, 1300 (1962)) attributes additional interest in our work designed to investigate either an equilibrium between or a resonance interaction between cyanocarbenes (I) and alkynylnitrenes (II).

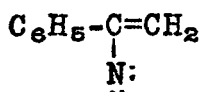


Dr. Selvarajan, who joined our group on November 1, 1966, has attacked this problem from two directions. He has carried out deoxygenation of benzoyl cyanide by a phosphine derivative and has begun preliminary work on the preparation of phenylnitrosoacetylene (unknown) and will plan to carry out its deoxygenation, also by a phosphine derivative:

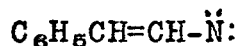


Evidence that deoxygenation of benzoyl cyanide has taken place consists in the formation of the corresponding phosphine oxide together with deoxygenation products which have not been positively identified. We prefer to report on their identification at a later time.

Dr. Krueger's work in vinyl nitrenes has become centered on the isomeric α - and β -phenylvinyl nitrenes (III and IV). His

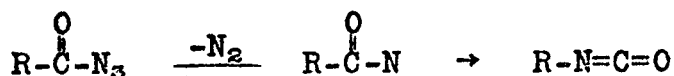


III

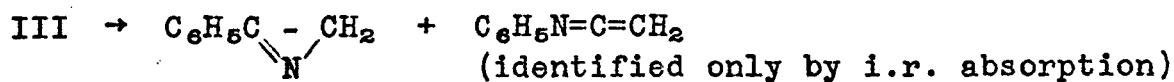


IV

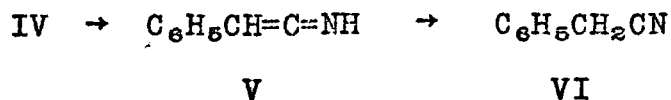
work is designed to elucidate the reaction which may require an intramolecular migration of a group or atom from an sp^2 carbon to an adjacent nitrene nitrogen. A classical example is found in the Curtius reaction (P. A. S. Smith, 'The Curtius Reaction' in Organic Reactions, Vol. III, John Wiley, 1947):



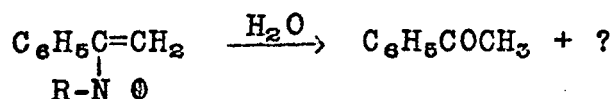
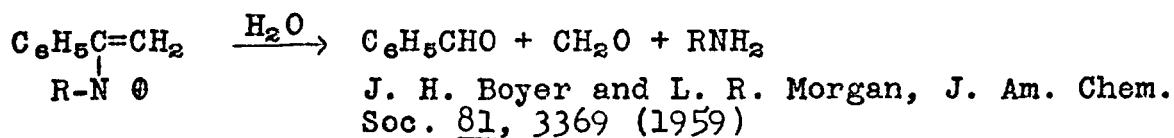
In contrast compound III gives predominantly intramolecular ring-closure (Smolinsky et al, J. Org. Chem. 27, 3557 (1962) with possibly trace amounts of the expected rearrangement:



We predict that compound IV will undergo rearrangement to a greater extent insofar as the rearranged product (V) may immediately tautomerize into a stable nitrile (VI):

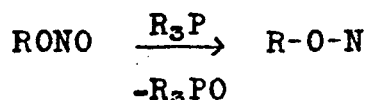


In related work Dr. Modler is investigating vinyl nitrenium cations. There appears to be two possible pathways for these ions to react with water:



Dr. Modler has discovered the second possibility and is following up with investigations designed to explain the mechanism and in particular, to clarify the relationship between the two reactions with water.

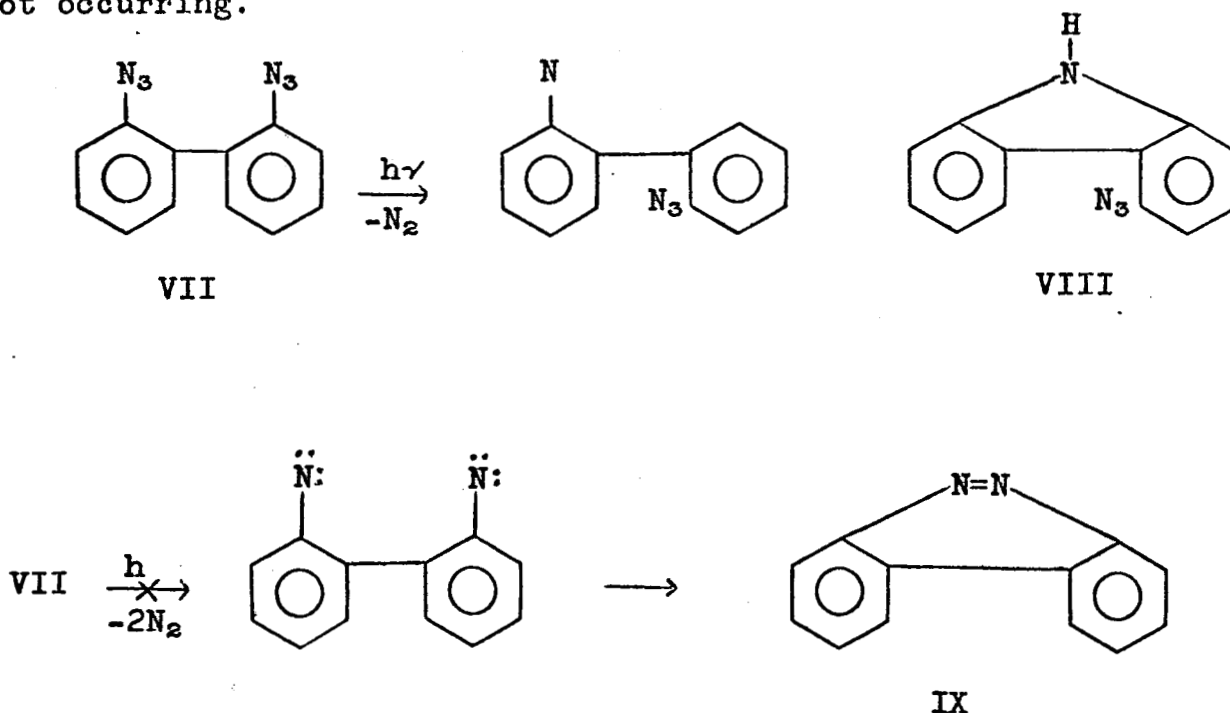
In September, Dr. Woodyard began an investigation of nitrenes in which the nitrene nitrogen is attached to oxygen. These oxanitrenes have not been reported in the literature. We have approached the problem by investigating the deoxygenation of alkyl nitrite esters:



Strong evidence that deoxygenation has occurred consists in the isolation of a phosphine oxide corresponding to the phosphine selected for the reaction. Some of the other products have been identified; however we are, at this time, puzzled by their

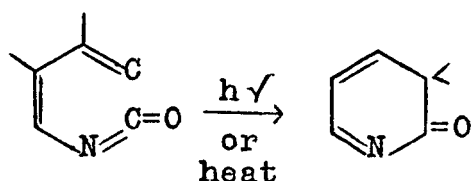
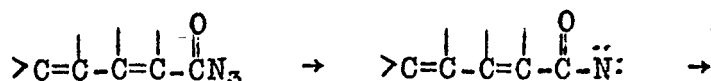
presence and prefer to make a more complete report later when we have a better understanding of the events which are taking place.

From his work in o,o'-diazidobiphenyl (VII) (previously unknown), Dr. Mikol has made the interesting discovery that photolysis apparently leads to a mononitrene rather than a dinitrene. Evidence for mononitrene formation consists in the low yield isolation of 4-azidocarbazole (VIII). The absence of benzocinnoline (IX) indicates that simultaneous photolysis of both azido groups with the formation of a dinitrene is probably not occurring.

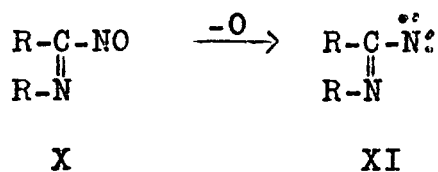


Dr. Mikol, who joined our group on October 1, is also investigating the preparation of diene isocyanates and their

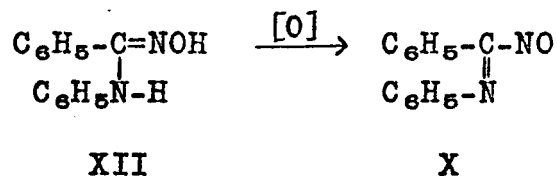
possible ring-closure by valence isomerization. The isocyanates may be prepared from corresponding acid azides via nitrenes:



To investigate azomethine nitrenes (XI), Mr. Paul Frints is initially studying the methods of preparing the nitroso azomethine derivatives (X). These may generate nitrenes (XI) on deoxygenation:



He is currently investigating the preparation of X by oxidation of appropriate amide oximes XII.



Several different oxidizing agents have been looked at. The results are not completely understood at this time and we prefer to discuss the results at a later time.

It is recognized that azomethine nitrenes (X) may also be produced by the pyrolysis of tetrazoles. We hope to develop a more general and less drastic reaction leading to their formation.